

Cermet coatings for solar Stirling space power

Donald A. Jaworske^{a,*}, Taylor Raack^b

^aNational Aeronautics and Space Administration, Glenn Research Center, Mail Stop 309-2, 21000 Brookpark Road, Cleveland, OH 44135, USA

^bNorthwestern University, Evanston, IL 60208, USA

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Abstract

Cermet coatings, molecular mixtures of metal and ceramic, are being considered for the heat inlet surface of a solar Stirling space power convertor. The role of the cermet coating is to absorb as much of the incident solar energy as possible. The ability to mix metal and ceramic at the atomic level offers the opportunity to tailor the composition and the solar absorptance of these coatings. Several candidate cermet coatings were created and their solar absorptance was characterized as-manufactured and after exposure to elevated temperatures. Coating composition was purposely varied through the thickness of the coating. As a consequence of changing composition, islands of metal are thought to form in the ceramic matrix. Computer modeling indicated that diffusion of the metal atoms played an important role in island formation while the ceramic was important in locking the islands in place. Much of the solar spectrum is absorbed as it passes through this labyrinth.

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1. Introduction

Solar Stirling convertors offer a space power option having the prospect of great longevity of operation, or operation in a high radiation threat environment, with little decrease in performance from beginning-of-life to end-of-life. In such a system, a solar concentrator would concentrate the Sun's energy on the heat inlet surface of a Stirling convertor, and the heat inlet surface would be coated with a high solar absorptance coating. The high solar absorptance coating would need to operate in the vacuum of space at temperatures approaching 450 °C and would have to exhibit durability in optical properties at these temperatures. Cermet coatings, molecular mixtures of metal and ceramic, are being considered for this application. Fig. 1 shows an artist's concept of a solar Stirling convertor, with the annular heat absorbing surface near the focus of the concentrator coated with a cermet coating. In this artist's concept, the heat

absorbing surface powers a 40-W convertor. The astronaut's gloved hand is provided for scale.

Early work identified the basic components needed to operate a heat engine in space [1]. The key optical components include a solar concentrator, a high solar absorptance coating at the heat inlet surface of the engine, and a radiator having a suitable optical coating or finish. A solar concentrator capable of concentrating sunlight by a factor of 300 is ideal. At lower concentrations, the temperature of the solar absorbing surface is too low for efficient heat engine operation, and at higher concentrations, cavity type heat receivers are more attractive. For a heat engine operating at 450 °C, a sharp transition in reflectance is desired at 1.8 μm, yielding simultaneously a high solar absorptance, α , and a low infrared emittance, ϵ . A radiator completes the heat flow through the heat engine by expelling waste heat.

Cermet coatings have been of interest in terrestrial solar power applications for years, particularly for trough style collectors. In one approach, a cermet-coated stainless steel tube is located in an evacuated glass tube along the focus of a trough. The heat absorbed by the cermet coating is transferred to the working fluid within the stainless steel

* Corresponding author. Tel.: +1 216 433 2312; fax: +1 216 433 2221.

E-mail address: Donald.A.Jaworske@nasa.gov (D.A. Jaworske).

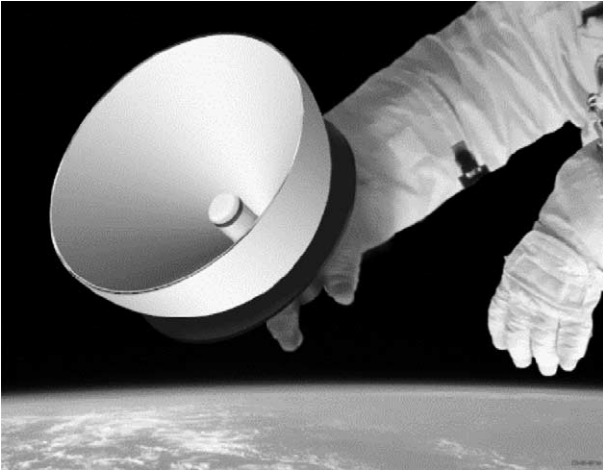


Fig. 1. Artist's concept of a solar Stirling convertor.

tube. Cost and durability are key factors for terrestrial solar power. Early coatings manufactured from nickel and nickel oxide have been shown to have an α/ϵ ratio of 3 [2]. Recent coatings of tungsten and aluminum nitride have been shown to have an α/ϵ ratio as high as 27 [3].

For solar Stirling applications, the working fluid is contained within a pressure vessel. The heat inlet surface is located near one end of the pressure vessel and the heat outlet surface is located near the other. A temperature gradient is established in the pressure vessel wall between the two temperature extremes. Based on typical wall thickness dimensions, the thermal properties of candidate pressure vessel materials, and pressure vessel geometry, the heat loss along the wall due to conduction was found to be comparable in magnitude to the heat loss due to radiation from the cermet-coated heat inlet surface.

The mechanism responsible for absorbing solar energy is of interest. Islands of metal are thought to form during the deposition process. These islands are eventually locked into place by the ceramic matrix yielding a labyrinth. The size of the islands, their distance from adjacent islands, and the population distribution of islands are thought to be responsible for the cermet coating optical properties. Tailoring this island forming process allows tailoring the optical properties of the coatings. This is achieved in practice by utilizing a sputter deposition target of varying metal and ceramic composition, and varying the time spent sputtering at each location.

This paper presents a summary of recent research, and is divided into three sections. Coatings were manufactured utilizing a variety of metal constituents, all in an aluminum oxide ceramic. A comparison of the as-manufactured optical properties of these coatings in the visible and infrared, covering the wavelength range of 0.25–25 μm is made. Candidate coatings on nickel substrates were subjected to heating in a furnace. The durability of these coatings after heating is reviewed, and the prospects of utilizing these coatings for solar Stirling applications are discussed.

Finally, computer modeling of the deposition process was performed utilizing a Monte Carlo technique. The deposition of metal and ceramic constituents, along with the diffusion of metal atoms and the formation of metal islands in a ceramic matrix, is discussed.

2. Materials and methods

2.1. Coating deposition

The cermet coatings discussed here were manufactured utilizing ion beam sputter deposition, described in detail elsewhere [4]. The coatings were purposely designed to be metal rich at their base and ceramic rich at their surface, and the metal and ceramic constituents were purposely graded through the thickness of the coating to promote metal island formation. This was accomplished by having the target constituents (the desired metal such as aluminum, nickel, titanium, platinum, copper or molybdenum and the desired ceramic such as aluminum oxide) placed on the surface of a cylinder, with the area occupied by the ceramic approximating a triangle on the surface of the cylinder. Initially, the ion beam was allowed to impinge on metal only. As the cylindrical target was rotated during deposition, the composition of the coating changed. A larger fraction of ceramic was exposed to the beam at the expense of the metal, and a larger fraction of ceramic was deposited. At the conclusion of deposition, the ion beam was impinging on ceramic only. In theory, the cylindrical target allowed for an infinite number of variations in metal and ceramic combinations through the thickness of the cermet coating. In practice, 11 discrete positions around the cylindrical target were typically used, yielding the approximate percentages of aluminum oxide summarized in Table 1, as determined by the geometry of the system. The metal constituent made up the balance.

Dwell time at each location on the target was a user-defined variable. In most cases, 7 min was spent at each location, yielding coating thicknesses in the range of 200–500 nm. A Dektak profilometer equipped with a diamond

Table 1

Percentage of aluminum oxide exposed to a 5-cm diameter ion beam, during cermet coating deposition

Sputter target position	%Al ₂ O ₃ , by volume
1	0
2	10
3	19
4	30
5	42
6	60
7	68
8	83
9	94
10	99
11	100

stylus was used to measure the thickness of coatings deposited on fused quartz witness coupons placed near the samples during deposition. The cermet coatings were deposited on both diamond-turned aluminum substrates 2.54 cm in diameter, and polished nickel substrates approximately 1 cm in diameter. Samples prepared on the diamond-turned aluminum substrates were used for optical properties evaluation, while samples prepared on the nickel substrates were used in the high temperature durability studies.

The solar absorptance of each sample was evaluated utilizing a Perkin-Elmer Lambda-19 spectrophotometer equipped with a 15-cm diameter integrating sphere. Total reflectance was obtained for each sample in the wavelength range of 0.25–2.5 μm . The reflectance value at each wavelength was subtracted from unity to yield absorptance at that wavelength and the absorptance values were weighted with respect to the air mass zero solar spectrum to yield a solar absorptance value. In this mathematical approach of calculating solar absorptance, the value is independent of temperature. The infrared emittance of each sample was evaluated utilizing a Surface Optics Corporation SOC-400t portable infrared reflectometer equipped with barrel optics. Infrared reflectance was obtained from each sample in the wavelength range of 2–25 μm . The reflectance value at each wavelength was subtracted from unity to yield emittance at that wavelength and the emittance values were weighted with respect to the black body spectrum at 450 °C to yield an infrared emittance value. In this mathematical approach of calculating infrared emittance, the value is dependent on temperature.

2.2. Heating

Sample heating was accomplished under flowing high purity nitrogen utilizing the furnace of a Perkin-Elmer DTA-1700 differential thermal analyzer. An individual sample was placed on top of two small graphite crucibles in the furnace. The thermocouples supplied by the manufacturer to measure temperature inside the furnace were adjacent to the bottom of the crucibles. The desired ramp and soak temperature profile was initiated using a programmable controller. The ramp rate for all samples was 20 °C/min. The four soak temperatures selected were: 460, 540, 610, and 680 °C. Time at soak temperature for all samples was 1 h. Cooling was accomplished through natural convection.

2.3. Computer modeling

A three-dimensional (3D) computer model was developed to study the formation of metal islands in cermet films in an attempt to relate their physical attributes and solar absorption profiles. The model was designed to simulate the creation of cermet films based on the kinetic Monte Carlo method, following closely the procedure described by Yang [5]. The core of the simulation is an event-driven process in

which two main events, particle deposition and diffusion, are processed alternately based on their probabilities of occurring within a finite time step. Individual deposition occurs at regular intervals based on the deposition rate specified for both metal and ceramic particles. After each deposition event, a varying number of diffusion events are processed based on the hop frequency of particles on the surface of the film.

Deposition events are processed by injecting either a metal or ceramic particle onto the film matrix. The actual ion sputtering process is approximated by a cosine distribution of incoming angles and above-surface injection locations. Classical dynamics equations are used to trace the trajectory of a particle to a vacant surface position in the simulated film, represented as a standard Ising lattice. The layer buildup of an experimentally created film allows for accurate representation of the small time interval between deposition events.

Diffusion events occur at a varying rate between two deposition events. Due to the relatively small diffusivity of the ceramic compared with the metal component, a modeling approximation was made to only process metal particles for diffusion. At the core of the diffusion event is the implementation of an n -fold algorithm for selection of a single particle to diffuse along the surface of the film. The diffusion rates for movements in six directions (nearest neighbor) are pre-calculated. These rates are stored in a variant B+ binary tree which propagates the total rate to the root of the tree. A stochastic priority algorithm selects one of the most likely surface particles to jump in the time step allotted. That particle performs one of its six jumps according to their own event probabilities. After a jump is performed, the neighboring particles' jump rates are updated. Diffusion events are repeatedly processed until the time for a new deposition event is reached. The number of diffusion events between any two deposition events typically varies from 10^2 to 10^5 based on the number of metal particles currently on the surface of the matrix and the formation temperature. Typical simulations begin with small numbers of diffusion events per deposition event and increase rapidly with growing numbers of metal particles injected.

Rates for diffusion jumps are calculated based on embedded atom method (EAM) jump barrier energies for nickel and copper [5]. These EAM energies are pre-calculated before the simulation and rely on molecular statics calculations of a single particle embedded in a matrix. EAM barrier energies are coordination-specific; particles have a much higher energy barrier to move from high to low coordination than from low to high. Boltzmann kinetics allow for the calculation of jump rates based on the jump barrier energies.

A computer software package containing this model was written to simulate the creation of these cermets according to varying deposition rates of metal and ceramic, formation temperature, and deposition time. The package allows for

single or multiple deposition rates to model actual deposition conditions and automation features to complete, record, and analyze multiple simulated cermet.

3. Results and discussion

3.1. Coatings

The six different metal constituents offered different optical properties as evaluated in both the visible and the infrared. Reflectance values from examples of the aluminum, nickel, titanium, platinum, copper and molybdenum cermet coatings, all on diamond-turned aluminum substrates, are summarized in Fig. 2. A low reflectance in the visible corresponds mathematically via Kirchhoff's Law to a high solar absorptance, while a high reflectance in the infrared corresponds mathematically via Kirchhoff's Law to a low infrared emittance. A sharp change in reflectance at $1.8\text{ }\mu\text{m}$ is desired, coupled with low reflectance values in the visible and high reflectance values in the infrared. Solar absorptance, infrared emittance, the α/ϵ ratio, and thickness values for the six coatings shown in Fig. 2 are summarized in Table 2.

In every case, infrared emittance at room temperature was found to be lower, yielding higher α/ϵ ratios. However, the operating temperature of the heat inlet surface of the solar Stirling convertor is envisioned to operate at $450\text{ }^{\circ}\text{C}$, hence, infrared emittance is reported at this temperature.

3.2. Heating

Of the six candidate materials, five were subjected to additional evaluation at high temperatures. The aluminum cermet was not put forward for heating owing to the low melting point of aluminum. As a first order approximation, diffusion of the metal islands in the ceramic matrix is thought to follow an Arrhenius relationship, with the rate of diffusion doubling with each $10\text{ }^{\circ}\text{C}$ increase in temperature. Hence, using the simple approach of exposing the samples to a temperature range of over $200\text{ }^{\circ}\text{C}$ provides an accelerated test of the durability of the coatings. Of course,

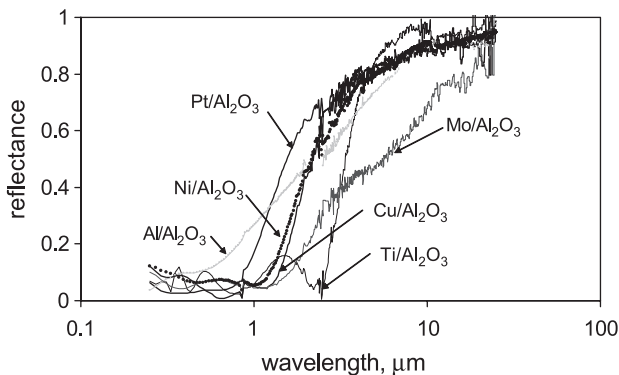


Fig. 2. Reflectance as a function of wavelength.

Table 2

Summary of optical properties and thickness of the cermet films, on diamond-turned aluminum substrates

Metal	α	$\epsilon_{450\text{ }^{\circ}\text{C}}$	$\alpha/\epsilon_{450\text{ }^{\circ}\text{C}}$	Thickness (nm)
Al	0.797	0.252	3	210
Ni	0.895	0.203	4	220
Ti	0.930	0.450	2	270
Pt	0.858	0.176	5	500
Cu	0.897	0.096	9	180
Mo	0.932	0.466	2	330

accelerated testing is best used as a guide and should be confirmed with actual testing over the long term.

Fig. 3 summarizes the solar absorptance durability of the coatings at the four temperatures. In each case, the absorptance values before heating were consistently uniform, indicating similarity among the samples initially. Of the five cermet coatings tested, the optical properties of three of the cermet coatings decreased substantially upon heating, at all temperatures tried. No pattern in the decline of solar absorptance is immediately discerned, suggesting that the deterioration in the optical properties occurred early in the heating process, and any diffusion of material causing the deterioration in optical properties was complete in a very short time. The two remaining cermet coatings exhibited desirable post-heating optical characteristics, those containing titanium and molybdenum. Future work on the development of barrier coatings may improve high temperature durability further.

3.3. Computer modeling

Analysis was performed on a 100×100 unit surface 20 units in height for 40 simulated seconds at 200 K. Deposition rates were purposely varied throughout the simulation. Metal deposition rates varied from 2500 particles injected per second to 0 particle injected per second. Ceramic deposition rates varied from 0 particle injected per second to 2500 particles injected per second. These parameters were scaled to accurately represent a microcosm of an experimentally created cermet film $2800\text{ }\text{\AA}$ thick, sputtered over 77 min, typical of those actually produced. The 100×100 unit surface of the simulated film was selected to reduce computer processing time to approximately 3 h on a commonly available desktop computer.

Simulations of the cermet film growth show varying sizes and shapes of 3D islands. Growth of islands is verified to be highly temperature sensitive [5]. At formation temperatures below 200 K, small metal islands are seen but rarely form a continuous lattice throughout the film. These islands are typically less than 10 particles in width, and they are often long and narrow. Diffusion increases drastically with higher temperatures, and metal particles relax on the surface to coordinate highly with surrounding metals. This leads to coalescence of much larger islands in

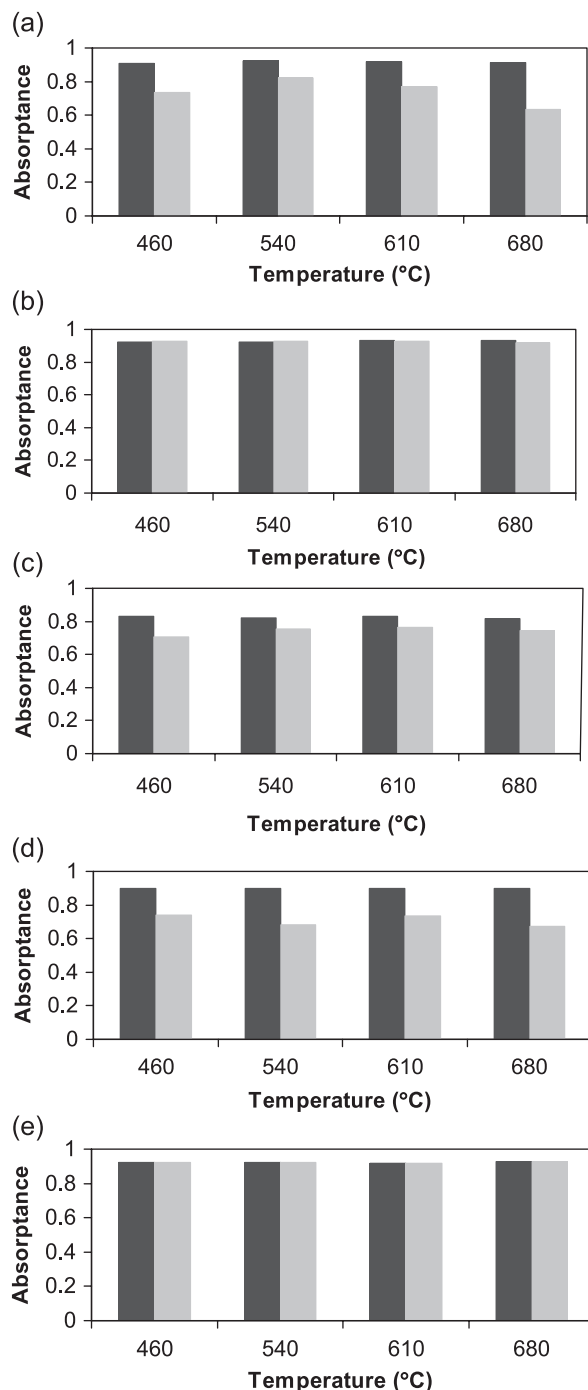


Fig. 3. Solar absorbance of (a) Ni/Al₂O₃, (b) Ti/Al₂O₃, (c) Pt/Al₂O₃, (d) Cu/Al₂O₃, and (e) Mo/Al₂O₃ before and after annealing as a function of temperature.

the cermet film. Most importantly the size of islands varies among different horizontal cross-sections of the film as seen in Fig. 4, often leading to metal island peaks and ceramic valleys in the vertical morphology of the film, as seen in Fig. 5.

Computer analysis of these films leads to an absorption coefficient for a layer of a film. Previous efforts have been made in other models to derive a particular effective

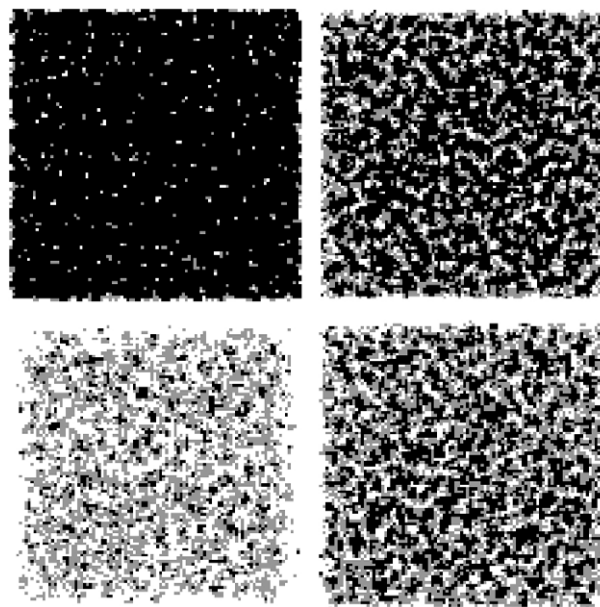


Fig. 4. Horizontal slices of a 100-width, 20-layer-thick simulated cermet coating. Black=metal, gray=ceramic. Clockwise from top left: Layers 1 (bottom), 4, 6, 11.

property (e.g. dielectric function or conductivity) for an entire layer, however, this method is only partially effective in describing optical properties [6]. An iterative analysis model has been adopted to generate finite absorption values of small cells of particles within a layer and use these cells to complete an overall absorption profile [6,7]. Typical absorption calculations involve the use of bulk dielectric functions in either Maxwell-Garnett or Bruggeman equations to solve for a composite dielectric function [8]. Yet these calculated dielectrics for simulated films often fail to describe experimentally created films adequately. Berthier et al. [6] described the morphology of cermets to be the major factor in their optical properties, more important than the metal to ceramic inclusion ratio or the respective variations in dielectric functions for any discrete cells.

This analysis studies patterns among metal networks directly for absorption. Absorption for a small cell is calculated based on the proportion of unit particle metal/ceramic interfaces to the total number of potential interfaces in the cell. As the analysis continues along the film, i.e., as the cell walks through the composite, local values for absorption are calculated and the individual absorption values are averaged to find the total absorption value. The size of the cell, a user-selected parameter in the software, is representative of the wavelength of light impinging on the coating. Smaller cells walking through the matrix are



Fig. 5. Vertical cross section of 100-width, 20-layer-thick simulated cermet coating. Black=metal, gray=ceramic.

analogous to visible light while larger cells walking through the matrix are analogous to the infrared. The macroscopic absorption values are not to be considered accurate representations of true solar absorptance of an individual film. Rather they are useful for comparing the relative solar absorption of cermet layers of various compositions and morphologies.

Analysis of model-derived cermets of varying compositions and formation temperatures indicates a strong correlation between films containing large-scale labyrinthine networks and high solar absorption. A macroscopic vertical slice of such a film, as shown in Fig. 5, reveals such a structure. This labyrinth permits full spectrum light to pass through its upper layers, but towards the lower layers of the film the light is caught among the many islands where most of the absorption takes place. Thus, it is important that larger islands do not completely coalesce to form a large block of metal, as this creates a more reflective solid barrier as opposed to an absorbent labyrinth.

The island structure of a film, and the gradation from small to large islands down through the thickness of the film, exhibits a pattern in calculated absorption. Absorption graphs of the individual layers of a simulated film show a common profile, as seen in Fig. 6. The upper most layers contribute little to the absorption, being mostly composed of ceramic. Layer absorption increases moving towards the bottom of the matrix, peaking at the layer with the highest metal/ceramic interface proportion. This layer is typically found between fifteen to twenty percent of the total height up from the bottom of the matrix. The lowest layers show a drastic decrease in absorption due to their high metal fraction which forms a reflective barrier to light. The absorption profiles for any layer in a simulated film are similar but scaled differently for all iterative analysis cell sizes.

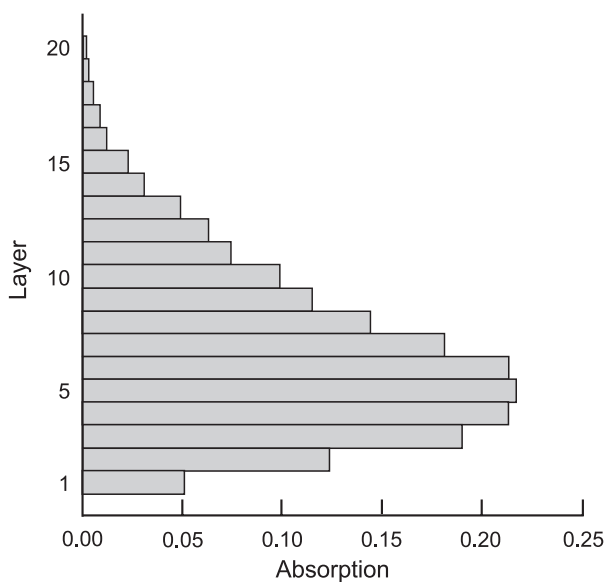


Fig. 6. Typical absorption profile for an absorbing layer in a 100-width, 20-layer-thick simulated cermet.

4. Conclusions

Cermet coatings, molecular mixtures of metal and ceramic, were prepared utilizing sputter deposition from custom made cylindrical targets of metal (aluminum, nickel, titanium, platinum, copper, and molybdenum) and ceramic (aluminum oxide). The coatings were typically 200 to 500 nm thick. Reflectance was measured over the wavelength range of 0.25–25 μm , and the solar absorptance and infrared emittance were calculated for each cermet type. Cermet coatings containing titanium or molybdenum, on diamond-turned aluminum substrates, had the highest solar absorptance, at 0.93. High temperature exposure of cermet coatings deposited on polished nickel substrates revealed that the titanium and molybdenum cermet coatings were also durable at temperatures as high as 670 $^{\circ}\text{C}$, under flowing nitrogen, for short durations. This observation suggests that these cermet coatings should be durable at a temperature of 450 $^{\circ}\text{C}$ for long durations. The solar absorptance of other candidate cermet coatings was found to be less durable at elevated temperatures.

Metal island formation in the ceramic matrix leading to the formation of a labyrinth structure through the thickness of the film is thought to be responsible for the observed solar absorptance characteristics. A computer model was developed to simulate the ion beam sputter deposition process and to show island formation in a 3D matrix. The computer model reveals that the key to island formation is diffusion of the metal particle on the growing surface of the film, with the coalescing metal particles being locked into place by the immobile ceramic constituent. Indeed, 10^2 to 10^5 diffusion events occur for each deposition event. The computer model also provides software to calculate an absorption coefficient, based on the number of metal/ceramic interfaces that a walking box encounters within the matrix. The calculated absorption coefficient reaches a maximum value at a position approximately twenty percent above the substrate interface, identifying the region of maximum metal/ceramic interfaces.

Thin film molecular mixtures consisting of titanium and aluminum oxide, or molybdenum and aluminum oxide, offer the best prospect for use on the heat inlet surface of a solar Stirling convertor. Such a convertor may provide energy to a spacecraft designed for high radiation threat orbits, and may exhibit great longevity of operation with little deterioration in performance from beginning-of-life to end-of life.

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